SOME ASPECTS OF THE SYSTEM

TITANIUM COBALT

G. R. PURDY

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THE UNIVERSITY OF ALBERTA

SOME ASPECTS OF THE SYSTEM TITANIUM COBALT

A DISSERTATION

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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ABSTRACT:

Microstructures and mechanical properties were qualitatively related for quenched and tempered titanium--7.5% cobalt alloys. The fully retained β structure produced by quenching had the best mechanical properties (170,000 psi and 9% elongation). A grain boundary transformation controls the tensile properties of subsequently tempered alloys. The stable tempered alloy displaying the best mechanical properties and the fully tempered alloy were subjected to short-time high-temperature tensile testing. A high temperature tensile testing apparatus was designed and built for this purpose.

The intermetallic compound Ti_2Co was studied by X-ray diffraction and metallographic techniques. The phase occurs off stoichiometric composition, with its greatest variation at high temperatures. The solubility limits of the phase have been determined, and an ammendment to the titanium--cobalt phase diagram is suggested.

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TABLE OF CONTENTS

		Page
I.	Investigation of the Relation Between Constitution and Mechanical Properties of a Titanium-Rich Alloy Containing 7.5 percent Cobalt.	
	Introduction	1
	Previous Work	2
	Apparatus and Experimental Techniques	4
	Preparation of Alloys	4
	Heat Treatment and Specimen Preparation	6
	Mechanical Testing	7
	High Temperature Tensile Testing	7
	Experimental Results	12
	Aging Tests	12
	Tensile Tests	12
	Activation Energy Calculation for Ti_2Co	22
	High Temperature Tensile Tests	27
	Discussion and Conclusions	27
II.	Investigation of the Intermetallic Compound Ti_2Co	31
	Introduction	31
	Apparatus and Experimental Techniques	31
	Experimental Results	33
	Discussion and Conclusions	40
	Bibliography	43

LIST OF TABLES

		Page
Table 1	Tempering Kinetics	14
2	Tensile Test Results	17
3	High Temperature Tensile Test Results	25
4	X-Ray Diffraction Results	34

LIST OF FIGURES

Figure		Page
1	Titanium - Cobalt Phase Diagram	3
2	Welding Apparatus	5
3	Assembly: High Temperature Tensile Testing Appartus	8
4	High Temperature Tensile Unit in Tensometer	10
5	Tempering Kinetics	13
6	Tensile Test Results	15
7	Tensile Test Results	16
8 to 19	Microstructures and Fractures of Quenched and Tempered Alloys	19 to 21
20	Activation Energy Calculation	23
21	High Temperature Tensile Test Results	24
22	Load - Extension Curves for Various Testing Temperatures	26
23 to 32	Microstructures Used to Establish Composition Limits for Ti_2Co	35 to 39
33	Portion of Phase Diagram	42

I. INVESTIGATION OF THE RELATION BETWEEN CONSTITUTION AND MECHANICAL PROPERTIES OF A TITANIUM-RICH ALLOY CONTAINING 7.5 PERCENT COBALT

INTRODUCTION

One of the aims of the physical metallurgist is to correlate constitution and mechanical properties of alloys. Due to the complexity of alloy systems, attempts to reach this ideal have met with varying success. At present the usual criterion for alloy selection is experience; but as more knowledge of transformations is obtained, the approach to alloy design and selection will become more fundamental.

Alloys and their heat treatments are chosen on the basis of strength, weight, machinability, or any other property pertinent to the use of the alloy.

When microstructures are examined, certain observations regarding phases present, phase dispersion, grain size etc. can be made. The observations become valuable tools for alloy design, since, for a given alloy system, a required set of mechanical properties will correspond to a definite microstructure.

Recently, the value of the short-time elevated temperature tensile test has been recognized. If an aircraft part is in service at low temperature, but is periodically required to withstand high temperature service, a knowledge of its short-time high-temperature characteristics is essential. This type of application does not require that the material be in equilibrium; only that it be in a relatively stable condition.

In this investigation, mechanical properties have been qualitatively related to microstructures that result from various heat treatments of an alloy of cobalt in titanium.

The portion of the constitutional diagram of interest in the present investigation is shown in figure 1. A eutectoid transformation occurs at 685°C and 7.5 percent* cobalt. The eutectoid composition was chosen for investigation.

Previous Work

Orrell and Fontana (1) found that alloys containing more than 6 percent cobalt fully retained the β phase (body-centered cubic) on quenching, while Swann and Parr (2), working with powder specimens, found that 10 percent cobalt was required to retain 100 percent β at room temperature. Similar differences occurred in work on titanium-iron (3) and titanium-nickel (4), and all are believed to be attributable to the effects of specimen size.

Taggart and Parr (5), working with a 2 percent cobalt alloy, related microstructural properties of quenched and tempered specimens to mechanical properties. This work involved an alloy which, on quenching, transformed to α' (close-packed-hexagonal), not to retained β.

The short-time high temperature tensile test has been extensively developed by the U.S. Steel Corporation of Delaware Research Laboratory (6). The specimen used was large (1/2 inch diameter), and was heated in air.

Jenkins and Mellor (7) have described an apparatus for making

* atomic percent is used throughout this dissertation

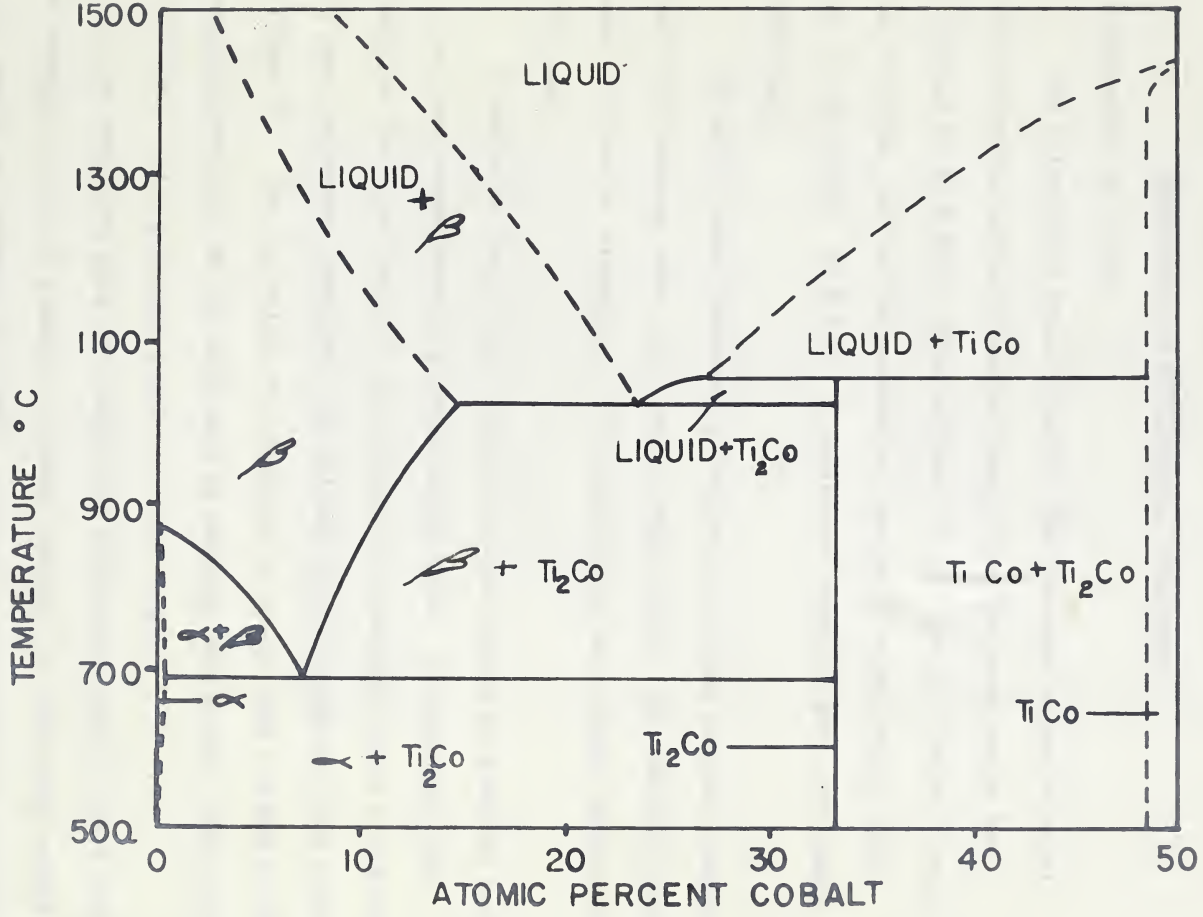

FIG. 1 TITANIUM-COBALT PHASE DIAGRAM after Orrell and Fontana

short-time high temperature tests in vacuum. The specimen was contained in a silica tube which was surrounded by an electrical resistance furnace. No extensometer was used.

APPARATUS AND EXPERIMENTAL TECHNIQUES

Preparation of Alloys:

The alloys were prepared using spectroscopic standard cobalt and levitation melted Japanese Sponge Titanium stock which had a hardness of 90 D.P.H. (The hardness of high purity Iodide Titanium is 70 D.P.H., while the hardness of sponge titanium ranges from 80 to 130 D.P.H. 90 D.P.H. is considered sensibly pure for sponge titanium.)

The alloys were obtained by levitation melting weighed charges, and chill casting them into a split copper mold. The resulting ingots were 1/2 inch in diameter, 1 1/2 inches long, and weighed approximately 20 grams.

In order to facilitate fabrication, the ingots were welded together in an inert atmosphere to produce longer rods. An induction coil supplied localized heat to the section to be welded, while a jig designed to apply pressure throughout the welding process supported the ingots (figure 2). The top weight was designed to slide down the two pillars, applying pressure to the weld zone as melting took place. The ingots provided a third suspension point for the weight.

The resulting rods (5" long) were fabricated into 1/4 inch rods by swaging in air (6 passes). Between passes, the rods were heated in a vacuum of 10^{-4}mmHg to 850°C. Usually, 6 heatings were sufficient to complete the swaging operation.

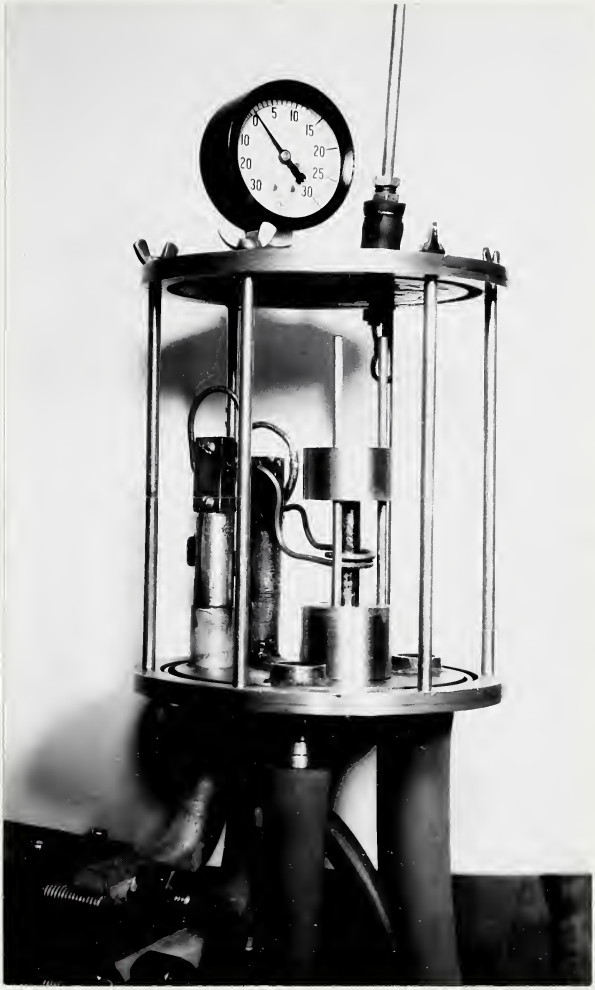

Fig. 2 Welding Apparatus

Specimen Preparation and Heat Treatment:

Tensile specimens were standard Hounsfield Tensometer number eleven specimens with cross-sectional area of 1/80 square inch and a parallel reduced length of 1/2 inch. Specimens for hardness measurement were cut from 0.15 inch diameter rods.

The specimens were machined from the swaged 1/4 inch bar and water quenched from the β range after soaking for 10 minutes at 830°C. In order to ensure a rapid quench, a special quenching furnace employing an argon atmosphere was used (8). Each quench was accompanied by a titanium standard. The hardness of this standard was determined after quenching as a check against contamination.

The specimens were tempered in sealed silica tubes filled with enough argon to produce a pressure of one atmosphere at temperature. At temperatures above 500°C, the specimens were wrapped in molybdenum foil to prevent contamination by the silica.

Specimens for hardness measurement were tempered for 1, 10, 100 and 1000 minutes at 350, 425, 500, 575 and 650°C. Each specimen was mounted, electrolytically polished and microscopically examined. Diamond pyramid hardness (3 Kg load) traverses were made from center to edge of the polished surface using a Tukon Hardness Tester. Five hardness values were taken for each of the 23 specimens. No appreciable center-edge variations were found.

Tensile specimens were quenched, then tempered 10 minutes at 350, 425, 500, 575, and 650°C. A second series of tests was carried out at the maximum tempering temperature (650°C) for tempering times of 1, 10, 100 and 1000 minutes.

A strain rate of 0.0225 inches per minute was employed for all tensile tests. No extensometer was used.

With each tensile test, a graphical record of load versus extension was obtained from the Tensometer. Total elongation of the test piece was measured after fracture had occurred. Reduction in area was measured whenever a significant reduction occurred.

High Temperature Tensile Tests:

In order to determine the short time elevated temperature characteristics of the alloy, a high temperature modification to the Hounsfield Tensometer was designed and built.

The apparatus was designed for use at temperatures up to 1000°C. The thermal gradient along the parallel length of the specimen was not to exceed 10°F in accordance with A.S.T.M. specifications (9).

An inert atmosphere was deemed necessary due to the high affinity of titanium alloys for exygen, nitrogen and hydrogen from water vapour. An oxide layer on the specimen would undoubtedly have an appreciable effect on the tensile properties of the small sample used. Further, oxygen, nitrogen, and hydrogen diffusing into the sample would alter its composition, and, therefore, its mechanical properties.

Referring to figure 3:

The specimen (a) and furnace were enclosed in a brass chamber (b). Load was applied by means of pull rods (c) and chucks (d) sealed into the argon chamber by dynamic O-ring seals (e). The pull rods were water cooled. The argon chamber was sealed by a tight fitting dynamic O-ring (f) and supported on the Tensometer members by a formed brass strip.

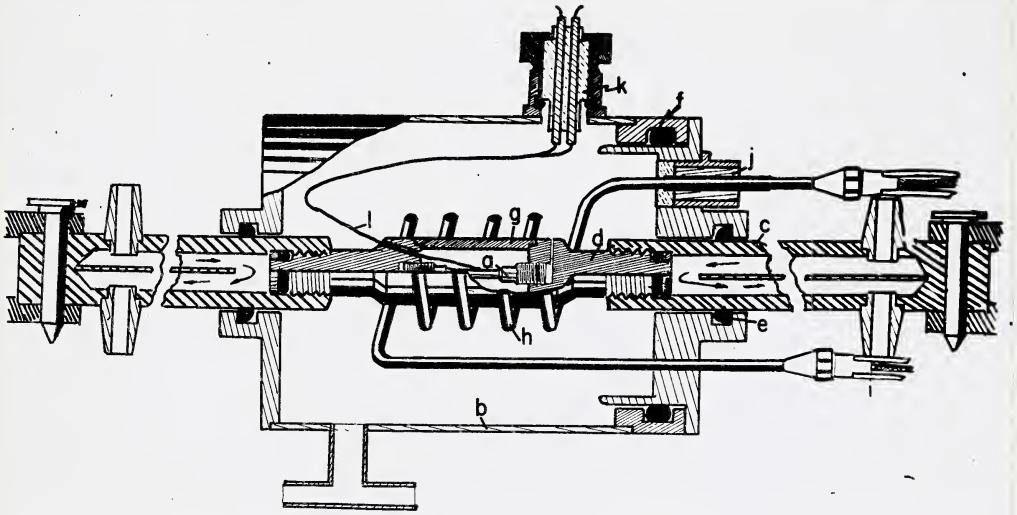

FIG. 3 HIGH TEMPERATURE TENSILE TESTING APPARATUS - ASSEMBLY

In order that possible contamination of the specimen be minimized, ceramic furnace components were avoided. The specimen was heated by a cylindrical molybdenum radiation element (g) which was heated by induction (h). This system was designed to reduce the "shading" common in induction heating. The radiation element also acted as an oxygen getter. Flexible high frequency leads (i) were made from braided copper sheathing inserted in clear flexible plastic hose. The water and high frequency current were introduced into the induction coil by copper leads insulated from the chamber cover by bakelite and epoxy resin (j).

Epoxy resin was cast around copper rods to form vacuum tight leads (k) for two thermocouples. The epoxi resin cylinder was sealed into the argon chamber by o-ring gaskets.

Materials employed in the construction of the high temperature parts were as follows:

Pull rods --- 18-8--Mo stainless steel
Specimen chucks:
Molybdenum - half percent titanium alloy (Tensile strength 60,000 psi at 2000°F)

The temperature was measured with a chromel-alumel thermocouple (l) bound to the specimen with fine molybdenum wire. Ample control ($\pm$ 2°C) was provided by the coupling control of the high frequency power supply.

The thermal gradient was measured by binding two thermocouples to the specimen--one at the middle and the other at the end of the reduced section. In no case was the thermal gradient found to exceed 10 °C.

Fig. 4 High Temperature Tensile Testing Unit
Shown in Hounsfield Tensometer

Axial loading of the specimen was ensured by the spherically seated pull rods in the Tensometer.

The specimens were made by threading a length of 1/4 inch bar, then machining shoulders and a parallel length in the center of the threaded portion. Except for the threaded ends, the specimens were standard number eleven Hounsfield Tensometer test pieces. All specimens were soaked at temperature in the testing apparatus for 10 minutes before testing. A strain rate of 0.0225 inches per minute was used for all high temperature tests.

The choice of heat treatment of the material tested was governed by the desire for good mechanical properties and reasonable elevated temperature stability. Room temperature tensile tests were used to judge the alloy constitutions likely to display good mechanical properties at high temperature, and tempering studies (figure 5) indicated the relative stability of the constitutions. The two conditions chosen for high temperature study were:

1) Quenched, tempered 100 minutes at 650°C. (good properties, stable)
2) Quenched, tempered 1000 minutes at 650°C. (Fully annealed).

An estimation of the decay of the modulus of elasticity with increasing temperature was attempted. The extention shown on the tensometer record includes the extension of the temsometer members. To determine the extent of this extension (which is constant for any given load), the tensometer was calibrated with a steel specimen.

The modulus of elasticity was estimated for each testing temperature.

EXPERIMENTAL RESULTS

The study of tempering kinetics based on hardness measurements and tensile tests yielded the results shown graphically in figures 5, 6, and 7, and in tabular form in tables 1 and 2.

Figures 8 to 19 show typical microstructures and the associated types of tensile fracture.

The as-quenched specimens yielded a single phase retained-β structure (figure 8) which had a hardness of 390 D.P.H. This structure yielded the best combination of mechanical properties (170,000 psi tensile strength and 9% elongation) of any of the conditions tested. The failure was transgranular (figure 9).

Figure 5 indicates an age hardening reaction during the early stages of tempering. Because of this reaction, the retained-β alloy would, if subjected to short-time high temperature tensile testing, age rapidly during the soaking period prior to testing, and during the test itself. The hardness would follow the tempering curve corresponding to the chosen testing temperature. If the alloy were used in a situation requiring short-time high temperature service, its constitution and mechanical properties would be significantly altered when the part returned to normal operating temperature. For this reason, the as-quenched alloy was deemed unacceptable for high temperature study.

The age hardening was attributed to the appearance of the ω phase (2), a metastable phase formed in several alloys of titanium with transition elements during β phase decomposition.

The alloy tempered for 10 minutes at 350°C remained homogeneous (figure 10) and exhibited a transgranular fracture (figure 11).

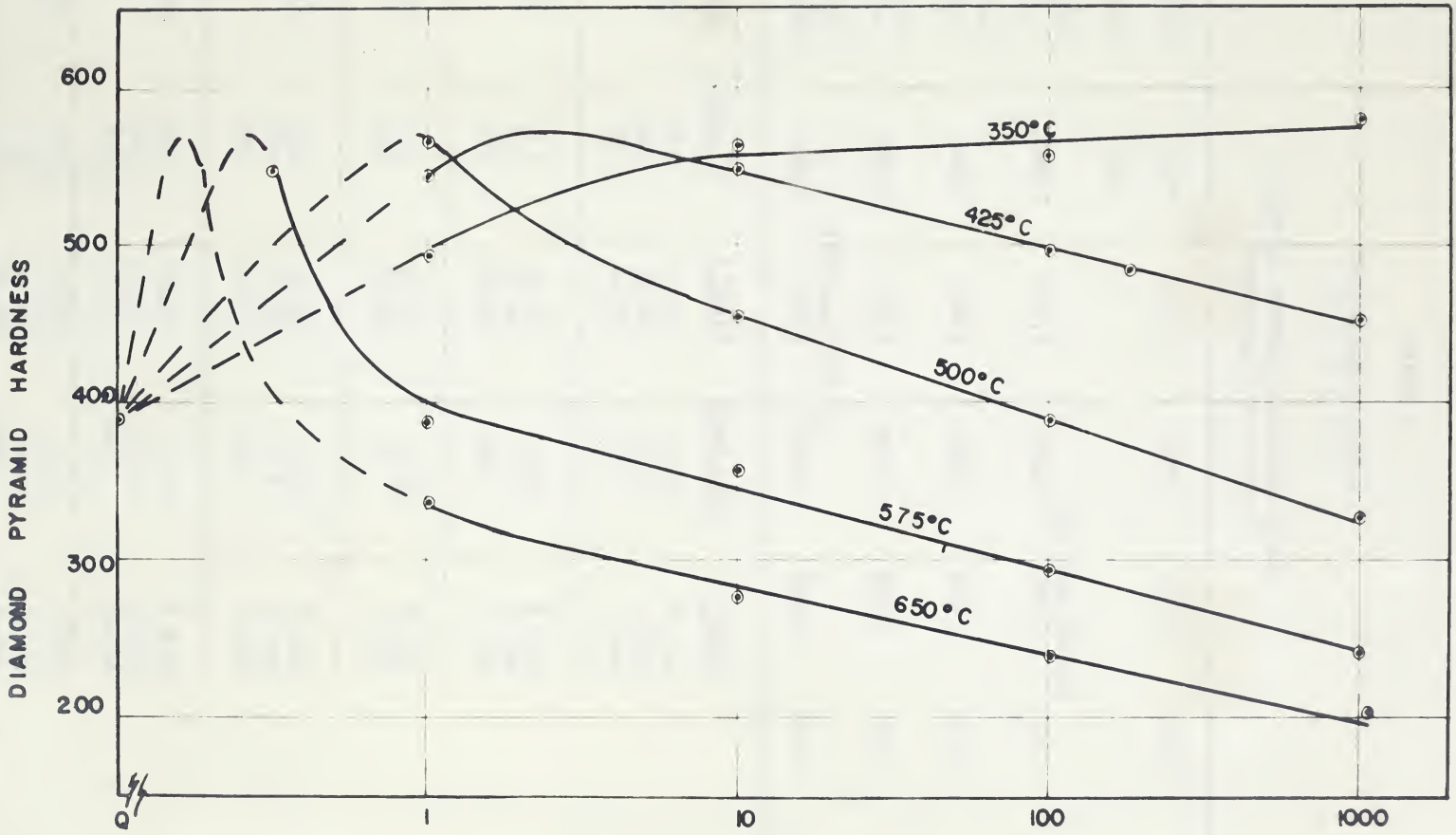

FIG. 5 TEMPERING KINETICS – 7·5 % Cobalt

TABLE 1

Tempering Kinetics
(7.5 at % Co:)

Diamond Pyramid Hardness Values
Tempering Temperature

Condition	350°C	425°C	500°C	575°C	650°C
Quenched	388.2				
Tempered 1 min.	490.5	541.2	560.7	(20 sec.-546.3) 385.2	335.7
Tempered 10 min.	560.6	548.7	452.4	355.7	275.0
Tempered 100 min.	555.2	497.1	387.6	292.2	238.5
Tempered 1000 min.	586.8	(180 min.-483.1) 451.2	328.2	240.6	202.5

D.P.H.	Temp.°C	$1/Tx10^4$	Time (min)	$\log_{10}t$
525	575	11.79	0.35	$\bar{1}$.544
	500	12.94	1.8	0.255
	425	14.33	25	1.398
475	575	11.79	0.45	$\bar{1}$.653
	500	12.94	5.0	0.698
	425	14.33	280	2.443
425	575	11.79	0.66	$\bar{1}$.820
	500	12.94	27	1.431
375	650	10.83	0.44	$\bar{1}$.644
	575	11.79	2.5	0.398
	500	12.94	156	2.193
350	650	10.83	0.70	$\bar{1}$.845
	575	11.79	7.5	0.875
	500	12.94	400	2.602
325	650	10.83	1.2	0.080
	575	11.79	22.8	1.358
	500	12.94	1000	3.000

D.S.H.

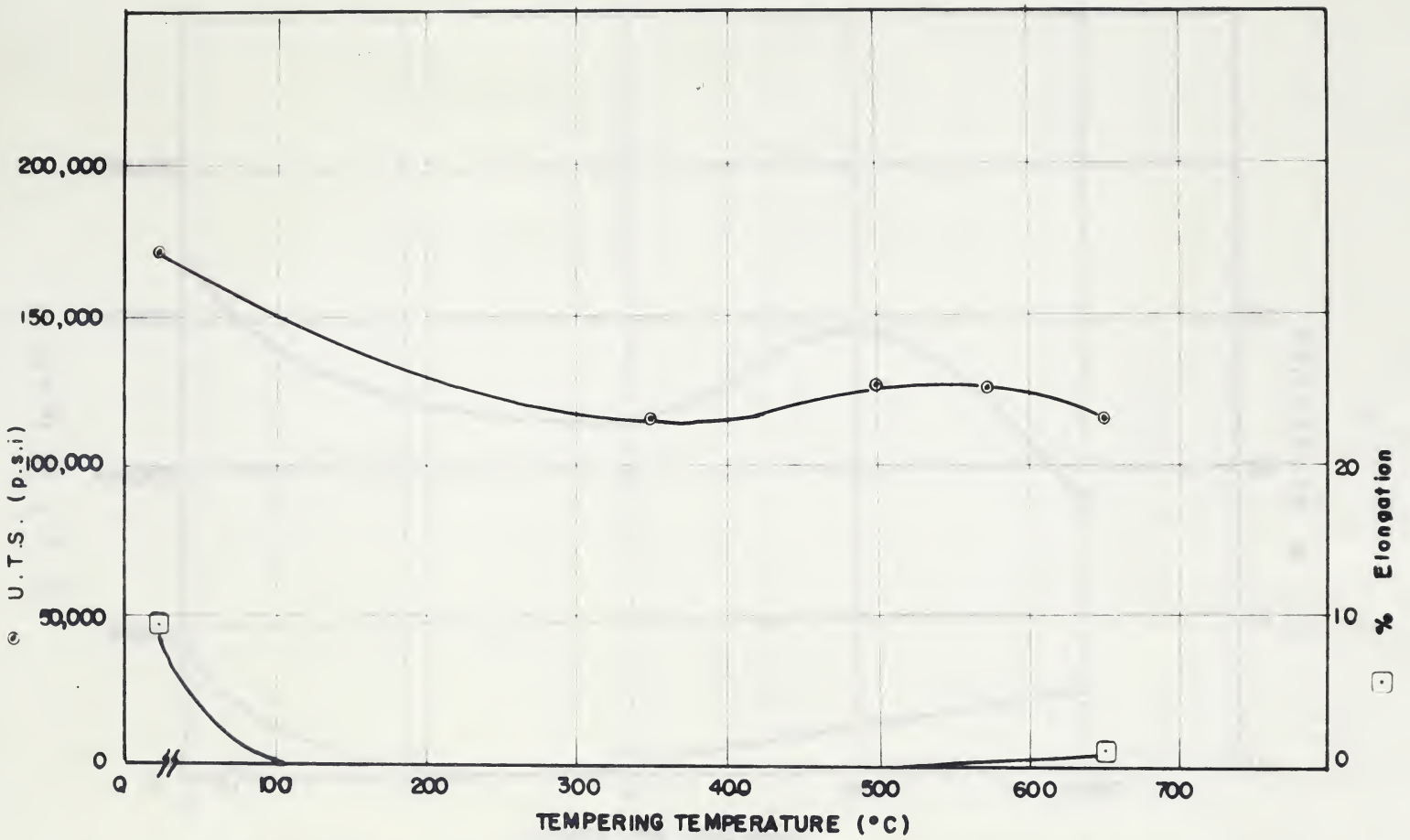

FIG. 6 TENSILE PROPERTIES of QUENCHED and TEMPERED SPECIMENS (Tempering Time 10 min.)

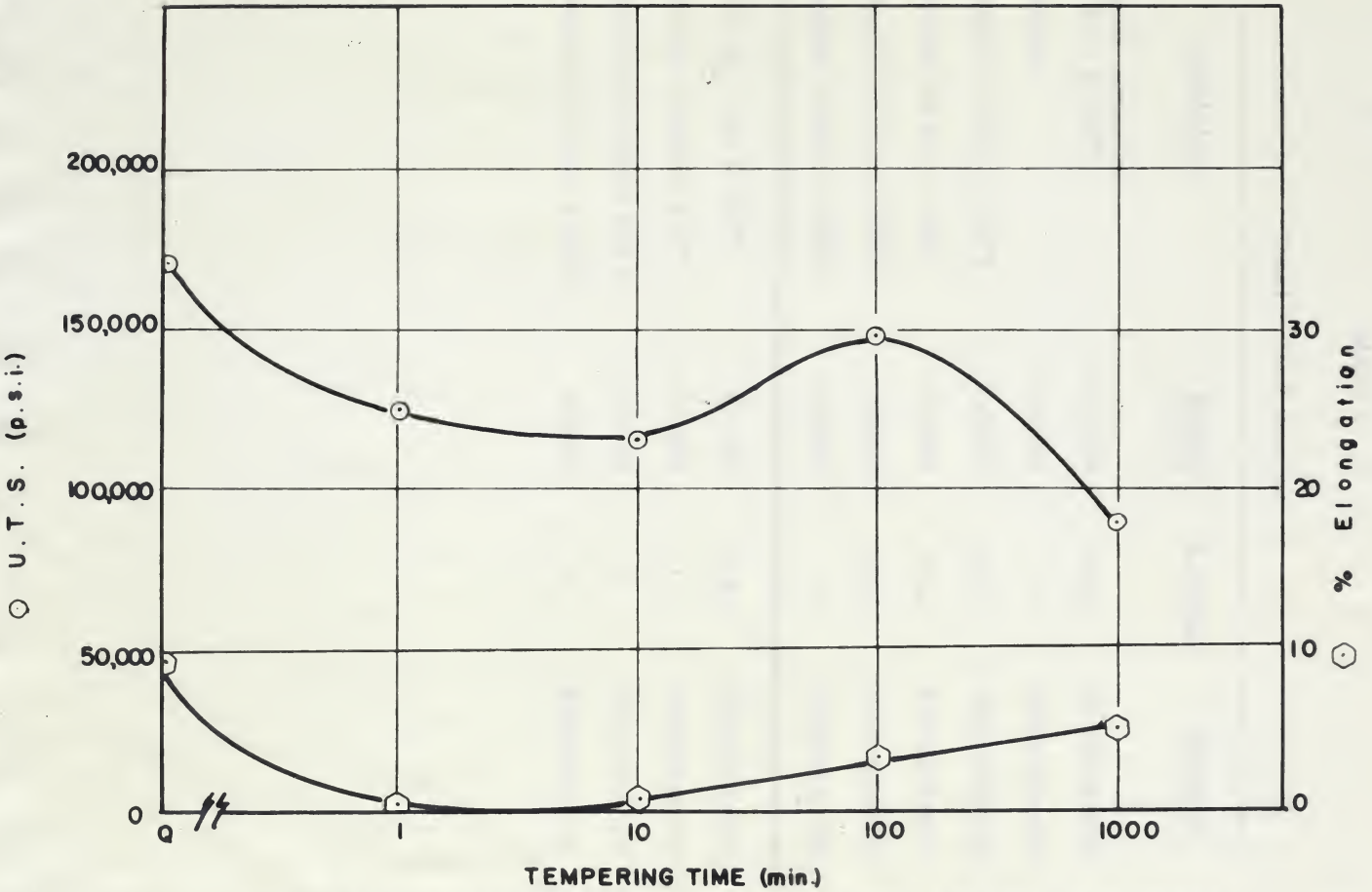

FIG. 7 TENSILE PROPERTIES of QUENCHED and TEMPERED SPECIMENS

(TEMPERING TEMPERATURE 650 °C)

TABLE 2

Tensile Test Results

Condition	U.T.S. (p.s.i)	% Elong	Fracture
Swaged, Annealed 30 min. @ 900°C	121,900	neg.	Intergranular
Quenched	170,000	9%	Transgranular
Tempered 10 min @ 350°C	115,000	neg.	Transgranular
Tempered 10 min @ 500°C	125,000	neg.	Intergranular
Tempered 10 min @ 575°C	125,000	neg.	Intergranular
Tempered 10 min @ 650°C	116,000	1%	Intergranular
Tempered 1 min @ 650°C	125,000	neg.	Intergranular
Tempered 10 min @ 650°C	116,000	1%	Intergranular
Tempered 100 min @ 650°C	147,000	3%	Intergranular
Tempered 1000 min @ 650°C	89,600	5%	Transgranular

Although the alloy was extremely hard (560 D.P.H.) it had a poor tensile strength (115,000 psi). Three specimens failed at the shoulder before a successful tensile test was realized.

As the time of tempering increased, the reaction involving ω ended, and further softening occurred due to the precipitation of Ti_2Co in α.

It will be noted from figures 12, 14, 16 and 18 that the grain boundaries offered the best nucleation sites for the precipitation of Ti_2Co in α, and the transformation proceeded inward from the grain boundaries.

The appearance of the grain boundary transformation coincided with a transition from transgranular to intergranular fractures in the tensile tests (figures 11, 13, 15).

Grain size, which is a significant factor in the mechanical behavior of this type of alloy, (3) was reasonably constant at 4 grains per square millimeter.

Tempering for 100 minutes at 650°C produced the greatest tensile strength of all tempered conditions. The ultimate tensile strength was 150,000 p.s.c. and the elongation was 3%.

Microscopic examination (figure 16) indicated that the grain boundary transformation had progressed until it represented an estimated one-third of the specimen volume. The grain boundary phase could be resolved at 2000X and proved to be a fine dispersion of Ti_2Co globules in an α matrix. The grain interiors had not yet completely transformed. The fracture was again intergranular, and observation of a fracture section indicated that the specimen had failed through the grain boundary phase. Microhardness measurements made with a Reichert micro-

Fig. 8 As quenched structure
Etchant 2% HF, HNO_3 wash
(X 150)

Fig. 9 Transgranular
Fracture
(X7)

Fig. 10 Tempered 10 minutes
at 350°C
Etchant 2%HF, HNO_3 wash
(X 150)

Fig. 11 Transgranular
Fracture
(X 7)

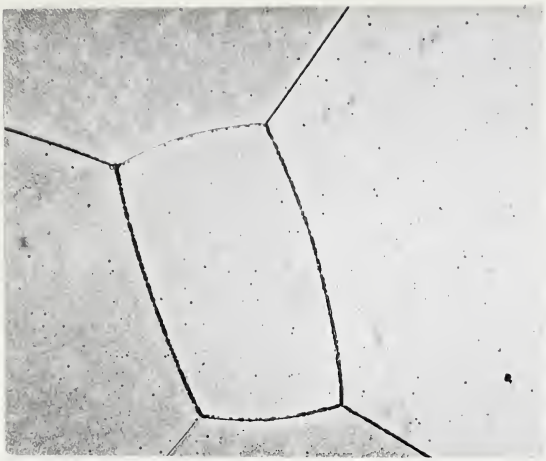

Fig. 12 Tempered 10 minutes at 500°C
Etchant 2% HF, HNO_3 wash
(X 150)

Fig. 13 Intergranular Fracture
(X 7)

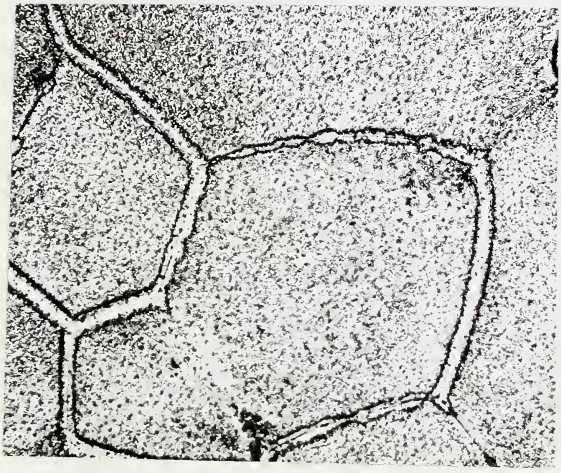

Fig. 14 Tempered 10 minutes at 650°C
Etchant 2% HF, HNO_3 wash
(X 150)

Fig. 15 Intergranular Fracture
(X 7)

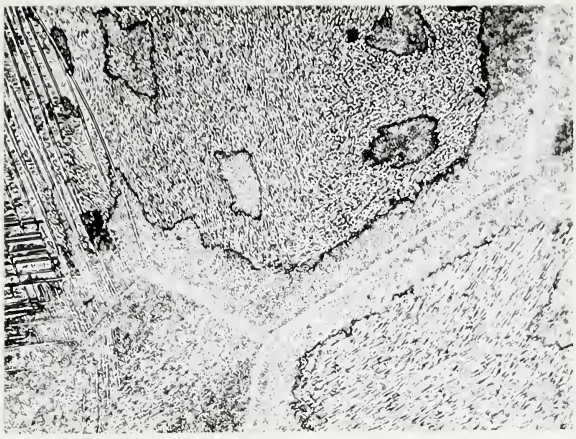

Fig. 16 Tempered 100 minutes at 650°C
Etchant 2% HF, HNO_3 wash
(X 150)

Fig. 17 Intergranular Fracture
(X 7)

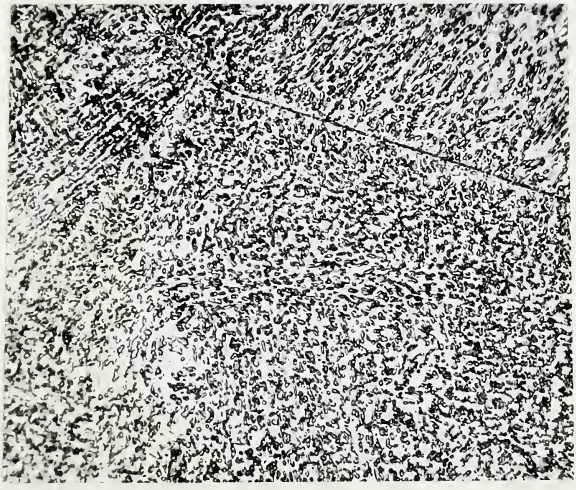

Fig. 18 Tempered 1000 minutes at 650°C
Etchant 2% HF, HNO_3 wash
(X 500)

Fig. 19 Transgranular Fracture
(X 7)

hardness tester (20 gram load) showed a hardness of 250 D.P.H. at the grain boundaries and 300 D.P.H. at the grain interiors.

The fully tempered condition (figure 13) yielded a homogeneous coarse dispersion of Ti_2Co globules in an α matrix. It was characterized by a low tensile strength (90,000 psi) and a reasonable ductility (5% elongation). The fracture was transgranular (figure 19).

Calculation of Activation Energy for Ti_2Co Precipitation:

A number of investigators (10) have shown that diffusion, tempering, creep and rupture, recrystallization and grain growth, appear to obey the rate process equation:

$$\text{Rate} = Ae^{-Q/RT} \text{---------} (1)$$

Where A is a constant,
Q is the activation energy,
R is the gas constant,
T is the absolute temperature.

Taking logs,

$$C = Q/2.3RT - \log t \quad \text{for a constant property.}$$

$$T \cdot (C + \log t) = Q/2.3R \text{ --------} (2)$$

Where $C = \log A$, a material constant.

If the hardness of an age hardenable alloy is plotted against time at a constant aging temperature, a steady decrease of hardness is observed after the hardening reaction is ended (as in figure 5). The softening reaction has been shown to depend on diffusion, a process to which equation 2 is applicable.

By applying the above theory to the results shown in figure 5, an activation energy was calculated for Ti_2Co (figure 20):

$$Q = 61{,}000 \text{ cal./mol.}$$

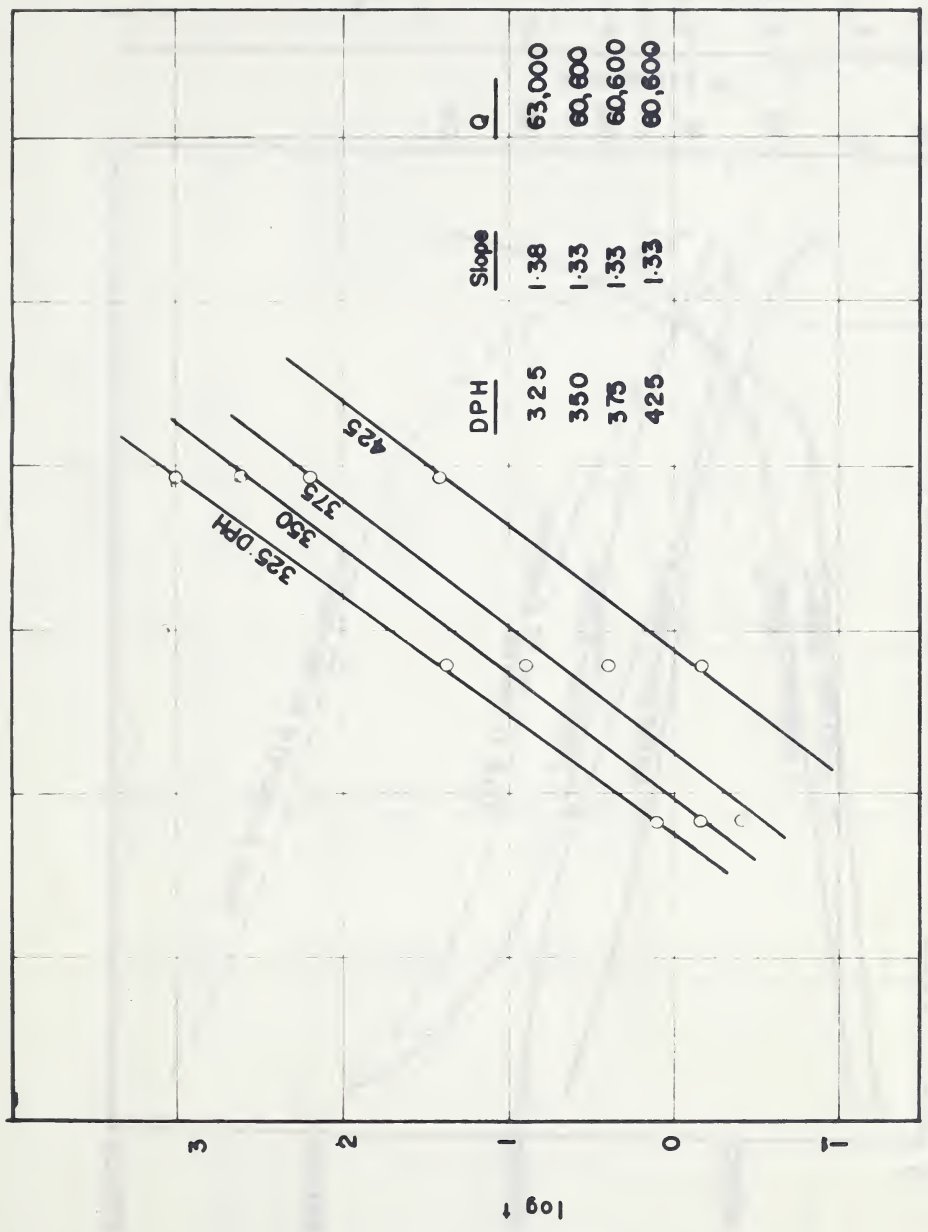

FIG.20 ACTIVATION ENERGY CALCULATION

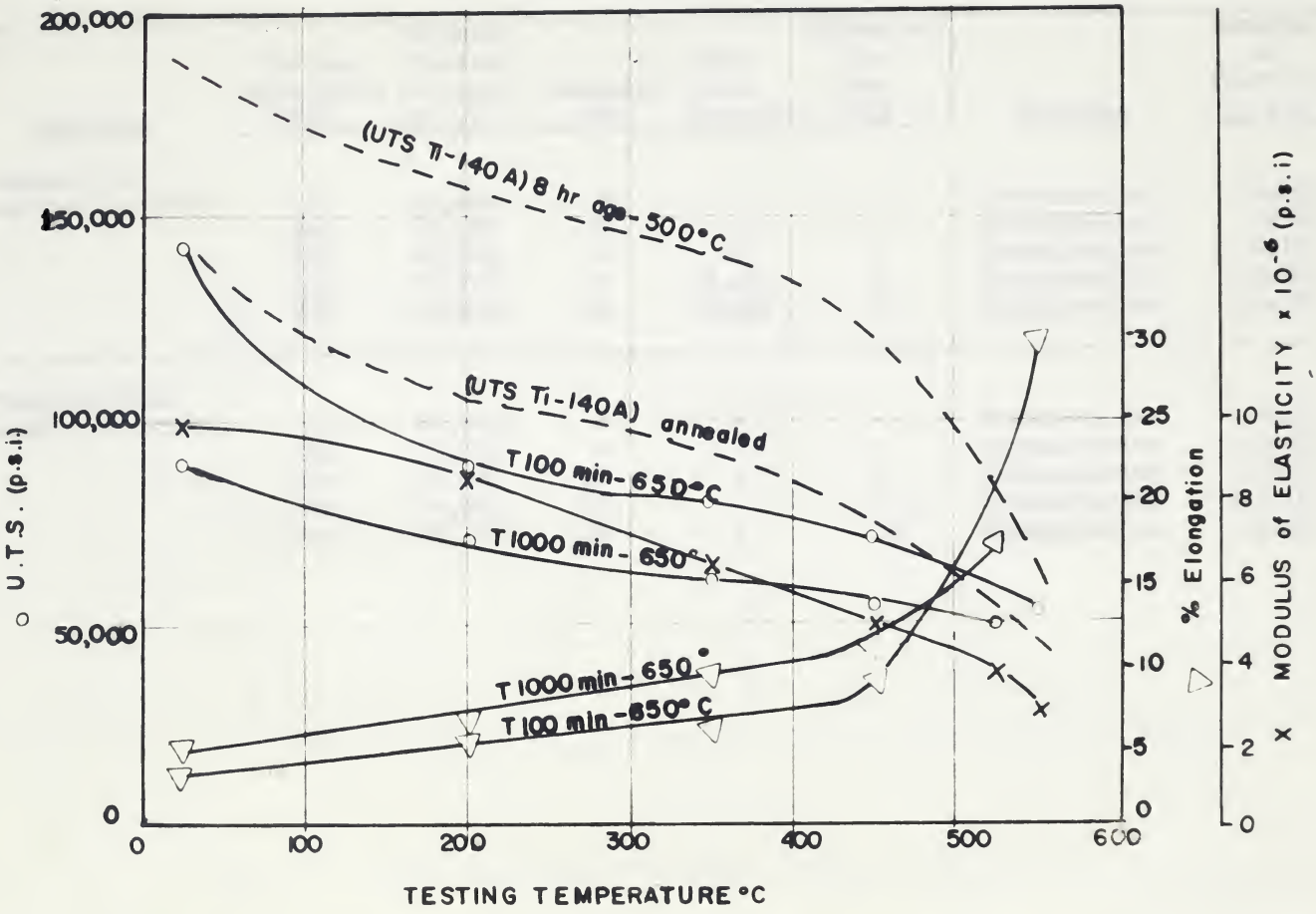

FIG. 21 - HIGH TEMPERATURE TENSILE TEST RESULTS (Ti-7·5 Co)

TABLE 3

High Temperature Tensile Test Results

Condition	Testing Temperature (°C)	Ultimate Tensile Strength (p.s.i.)	Elongation (%)	Yield Point (p.s.i.)	Reduction in Area (%)	Fracture	Modulus of Elasticity (p.s.i.)
Tempered 100 minutes at 650°C	20	147,000	3	-	-	Intergranular	10×10^6
	200	89,600	5	-	-	Intergranular	9×10^6
	350	80,500	6	-	-	Intergranular	5.5×10^6
	450	71,700	9	59,000	5	Transgranular	4.2×10^6
	550	53,800	30	36,000	30	Transgranular	2.9×10^6
Tempered 1000 minutes at 650°C	20	89,600	5	-	-	Transgranular	9.5×10^6
	200	71,700	6	-	-	Transgranular	8.5×10^6
	350	60,900	10	-	7	Transgranular	6.8×10^6
	450	55,600	11	-	13	Transgranular	5.5×10^6
	530	50,100	18	-	12	Transgranular	3.7×10^6

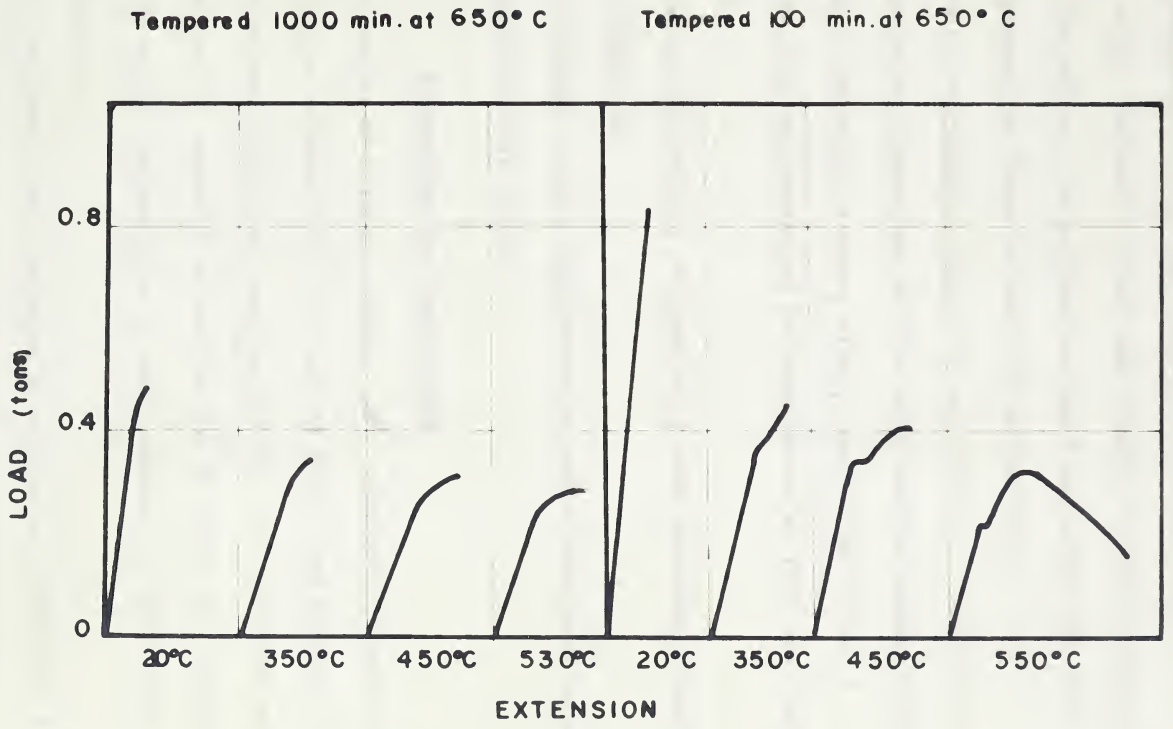

FIG. 22 LOAD–EXTENSION CURVES for VARIOUS TESTING TEMPERATURES

High temperature tensile tests were carried out on the two chosen conditions (Tempered 100 and 1000 minutes at 650°C). One test at 800°C (β range) indicated a very low tensile strength (approximately 4000 psi). Thereafter, the maximum testing temperature was 550°C, where the tensile properties began to drop off appreciably.

The results are shown in figure 21 and table 3. In order that the high temperature properties of this alloy may be compared to those of a comparable commercial ternary alloy, results for Ti-140 A (Ti--2Fe--2Cr--2Mo) as determined by Greenlee et al (11) are plotted in figure 21.

The decay of the modulus of elasticity with increasing temperature is shown in figure 21.

Figure 22 shows several load-extension curves obtained during high temperature tensile tests.

DISCUSSION AND CONCLUSIONS

The production of a fully retained β structure (figure 8) on quenching is in accordance with the work of Orrell and Fontana (1). The good mechanical properties associated with this structure would suggest that further research be carried out in order to stabilize this phase at higher temperatures by small amounts of additional alloying elements.

The age hardened alloy (tempered 10 minutes at 350°C) had a poor tensile strength (115,000 psi) despite its increased hardness. This low value was probably due to the extreme brittleness and notch sensitivity accompanying the high hardness.

The lines crossing the crystal faces in figure 10 are thought to be twins, since each line exhibits a definite width when examined at high power. The twinning is probably initiated by quenching strains.

An incubation period for Ti_2Co precipitation is implied by the microstructures, since no precipitate was observed during the early stages of tempering.

The grain boundary transformation shown in figures 12, 14 and 16 was observed by Swann and Parr in tempering studies of a 10 percent cobalt alloy. The extent of the grain boundary transformation after tempering 100 minutes at 650°C, and the fact that failure occurred through this phase indicates that the grain boundary transformation controls the tensile properties of the alloy. The appearance of the grain boundary phase coincided with a transition from transgranular failure to intergranular failure in the earlier stages of tempering.

Because of the apparent effect of the grain boundary phase, grain size may have a great effect on the mechanical properties of this alloy. A lower soaking temperature prior to quenching is possible for this eutectoid composition, and might result in a smaller grain size, which would probably improve ductility.

The grain boundary phase seen in figure 16 was similar to, but much finer than, the structure of the fully tempered alloy. The coarseness of the fully tempered structure is probably the reason for its low strength.

The activation energy for Ti_2Co precipitation (Table 1, figure 20) was calculated assuming that the ω-phase decomposition ended at the discontinuities in the tempering curves (figure 5) and that all subsequent

softening depended upon the precipitation of Ti_2Co in α . The value obtained (61,000 cal/mol) compares favourably with the value obtained by Swann and Parr (2) who used X-ray diffraction techniques and found Q to be 50,000 cal/mol. Since no data are available for the activation energy of diffusion of cobalt through the β phase, the rate controlling factor in the tempering process cannot be determined. However, the confirmation of Swann and Parr's work lends weight to the statement that the precipitation differs from that occurring in titanium-nickel alloys (12). The rate-controlling process for Ti_2Ni precipitation was reported to be the self-diffusion of titanium,--the only process that could account for the high activation energy obtained (84,000 cal/mol).

The activation energy calculation can be used to select an aging treatment to obtain a desired level of mechanical properties, and can be used to reduce the number of tests necessary to establish aging response.

The tensile test at 800°C yielded a very low tensile strength, indicating, perhaps, the possibility of good hot formability, but certainly showing that the alloy has no real design function at this temperature.

When Ti-7.5 Co is compared with Ti-140 A, it will be noted that that former alloy, while posessing lower room temperature strength, withstands short-time high-temperature service with a less marked reduction in strength.

The estimated modulus of elasticity at room temperature ($10 \pm 2 \times 10^6$psi) (figure 21) is very low compared with most structural alloys. However,

it is only slightly lower than values obtained for commercially pure titanium, (14 to 20 X 10^6 p.s.i.) (13).

The modulus decays rapidly as the testing temperature is increased, until, at 550°C, it has dropped to 3 x 10^6 p.s.i.

The load-extension curves shown in fugure 22 serve to more fully describe the tensile properties of the alloy. At higher temperatures, the specimens that had been tempered for 100 minutes at 650°C displayed a yield point, while specimens in the fully annealed condition had similar load-extension curves at all temperatures.

It will be noted from table 3 that the two specimens showing a well-defined yield point (tested at 450 and 550°C) failed through the grains, while those specimens not showing a yield point (tested at 20, 200, 350°C) displayed an intergranular fracture.

Since, at higher temperatures, the grain boundary phase no longer controls the tensile properties, a different failure mechanism must be operative.

II A STUDY OF THE INTERMETALLIC COMPOUND Ti_2Co

INTRODUCTION

The first intermetallic compound to appear at the titanium-rich side of the titanium-cobalt system was found by Laves and Wallbaum (14) to be Ti_2Co (figure 1). They described this compound as isomorphous with Ti_2Ni and Ti_2Fe, and demonstrated that it had a face-centered cubic structure with 96 atoms per unit cell. This contention is supported by the work of Duwez and Taylor (15) and by that of Orrell and Fontana((1).

Rostoker (16) believes that Ti_2Co does not exist, and that the phase considered by the other workers to be Ti_2Co is Ti_4Co_2C. However, Orrell and Fontana determined oxygen and nitrogen contents and found that their alloys did not contain sufficient of these elements to produce appreciable quantities of a stoichiometric oxygen compound.

Ti_2Co is generally agreed to have a face-centered cubic structure with 96 atoms per unit cell, and a lattice parameter of 11.30 Å.

Yurko et al (17), working with powder specimens from levitation melted alloys, determined that Ti_2Ni had a range of composition of 1 to 2 percent nickel at 700°C and a smaller range of composition at lower temperatures. X-ray and metallographic techniques were employed.

The present investigation was initiated in order to determine the composition limits of the phase Ti_2Co.

EXPERIMENTAL APPARATUS AND TECHNIQUES

Initially, five alloys were prepared by levitation melting. High purity iodide titanium and spectrographic standard cobalt were

used in each case.

The compositions produced were: 23.0% Co
31.0% Co
33.33% Co
36.4% Co
44.5% Co

These alloys were obtained as homogeneous, chill-cast ingots which were weighed after casting to ascertain that no material had been gained or lost during the levitation melting process. The non-equilibrium structures were microscopically examined.

In an attempt to produce equilibrium structures, filings from the ingots were equilibrated in molybdenum vessels in evacuated silica tubes for 15 minutes at temperatures just below the appropriate transformation temperatures (685°C for the low cobalt alloys and 1025°C for the high cobalt alloys). X-ray and metallographic examinations indicated that the holding time was not sufficient, and that non-equilibrium structures persisted.

Since the reaction appeared to be sluggish, the powders were equilibrated in a titanium bottle in a silica capsule, filled with argon at low pressure, for a period of five hours. This treatment, according to metallographic observation, produced the desired equilibrium structures.

X-ray diffraction plots were made of the powders (using Geiger spectrometer). A pure nickel standard was included with each sample, so that accurate parameter measurements might be made.

Portions of the ingots were equilibrated in argon-filled molybdenum-lined silica capsules for 20 hours, and X-ray plots were made

of the resulting structures. Again, the equilibrating temperatures were 650°C and 1000°C.

Because three attempts to produce a single-phase structure at 33.33% Co resulted in alloys containing some TiCo, a new series of 6 alloys was made. The ingots from the first melts were re-levitated in order to ensure homogeneity. The compositions were: 32.46% Co
33.00% Co
33.33% Co
33.56% Co
34.33% Co

Portions of these ingots were held for 100 hours at 1000°C, and quenched by breaking the silica capsules under water.

Since a single phase structure was observed in the 33.00% Co alloy, three more alloys were prepared using the techniques described above. The compositions were: 32.85% Co
33.00% Co
33.15% Co

Each ingot was held for 100 hours at 1000°C, then water quenched. Longitudinal sections of the ingots were examined to check for homogeneity. Portions of the quenched specimens were then equilibrated for 100 hours at 650°C, and water quenched.

Parts of the as-cast ingots containing 33.00 and 33.33 percent cobalt were held for 400 hours at 750°C, then water quenched.

All the resulting structures were studied by means of X-ray diffraction and microscopic techniques.

EXPERIMENTAL RESULTS

The results of the X-ray investigations are shown in table 4. The results indicate different compositions for Ti_2Co at high and low

TABLE 4

X-Ray Diffraction Results

Composition (at % Co)	Condition	θ°(333) (Co Kα radiation)	d (A)
23.0	Powder, annealed 650°C	24.33	
23.0	Ingot, annealed 650°C	24.32(5)	
31.0	Powder, annealed 650°C	24.32	
31.0	Ingot, annealed 650°C	24.32(5)	11.29
33.33	Ingot, annealed 650°C	24.32	
32.85	Ingot, annealed 1000°C, equilibrated 650°C	24.32	
36.4	Powder, annealed 1000°C	24.25	
36.4	Ingot, annealed 1000°C	24.24(5)	
44.5	Powder, annealed 1000°C	24.24	11.33
44.5	Ingot, annealed 1000°C	24.25	
32.85	Ingot, annealed 1000°C	24.24	

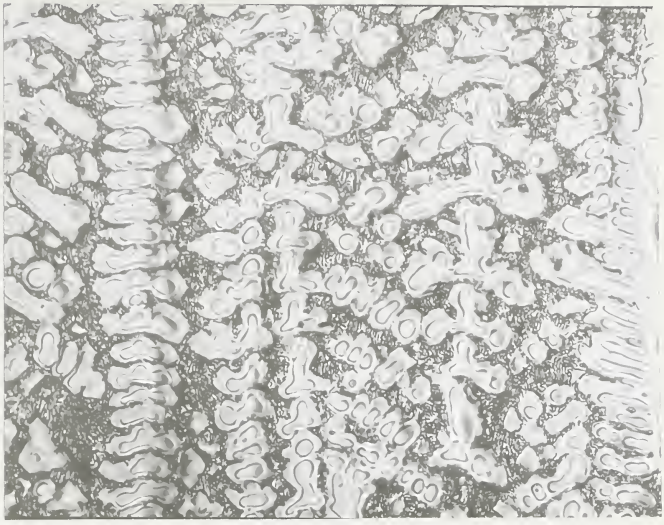

Fig. 23 33.33% Co As cast
Etchant 2% HF, HNO_3wash
(X 600)

Fig. 24 32.85% Co Held at 1000°C,
water quenched. (Ti_2Co + retained β)
Etchant 2% HF, HNO_3wash
(X 300)

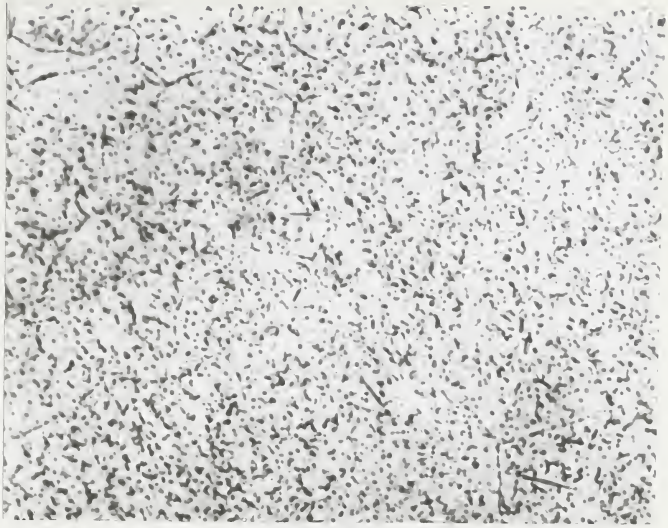

Fig. 25 32.85% Co Held 1000°C,
water quench, equilibrated 650°C (Ti_2Co + α)
Etchant 2% HF, HNO_3wash
(X 300)

Fig. 26 33.00% Co Held 1000°C,
water quench. (Ti_2Co)
Etchant 2% HF, HNO_3wash
(X 300)

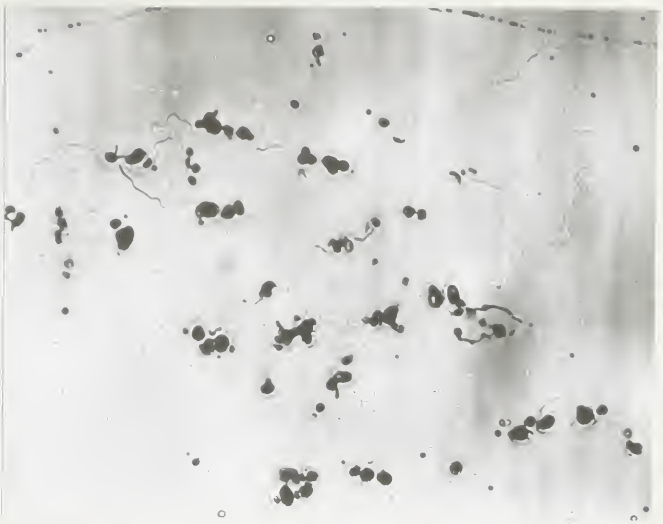

Fig. 27 33.00% Co, Held 750°C, quenched.
(Ti_2Co + retained β)
Etchant 2% HF, HNO_3wash
(X 300)

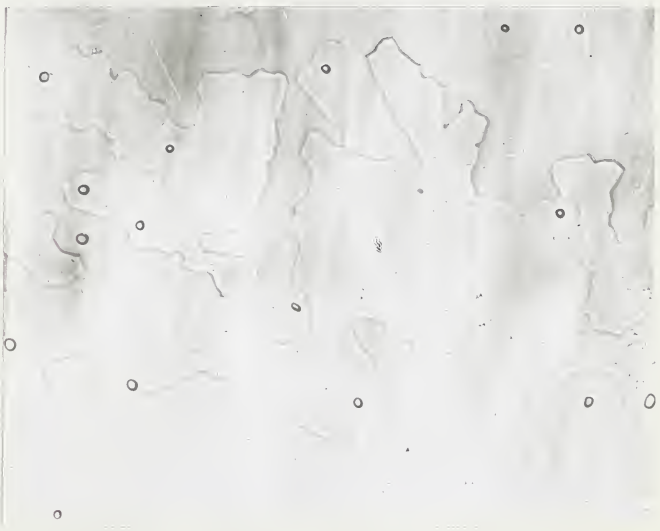

Fig. 28 33.15% Co, Held 1000°C, quenched
(Ti_2Co + TiCo)
Etchant 2% HF, HNO_3wash
(X 300)

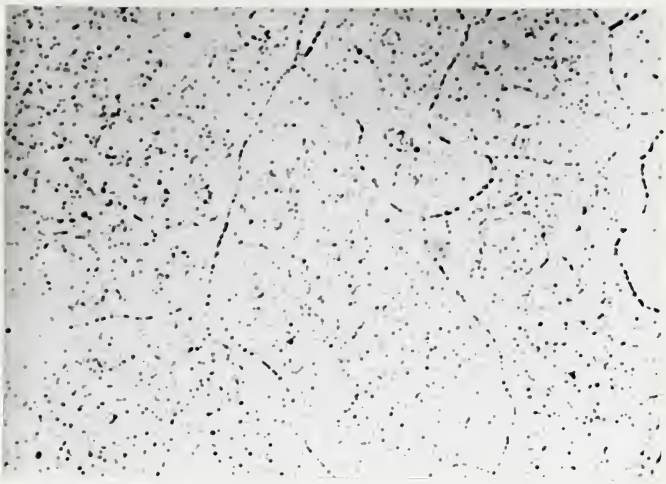

Fig. 29 33.15% Co, Held 1000°C, quenched, equilibrated 650°C (Ti_2Co + α)
Etchant 2% HF, HNO_3wash
(X 300)

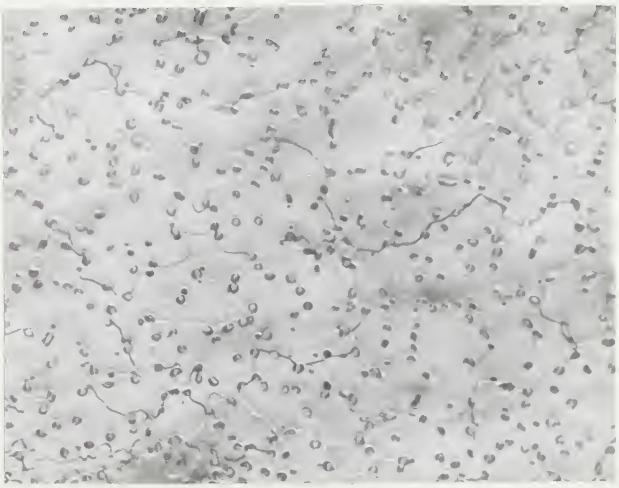

Fig. 30 33.33% Co, Held 1000°C, quenched
(Ti_2Co + TiCo)
Etchant 2% HF, HNO_3wash
(X 300)

Fig. 31 33.33% Co, Held 750°C, quenched
(Ti_2Co + TiCo)
Etchant 2% HF, HNO_3wash
(X 300)

Fig. 32 33.33% Co, Held 1000°C, quenched,
equilibrated 650°C (Ti_2Co + TiCo)
Unetched
(X 300)

temperatures. The high temperature form has a lattice parameter of 11.33 Å, compared with 11.29 Å for the low temperature form. (An accuracy of ±0.005 Å is computed for all parameter measurements.)

An approximate calculation (using Vegard's Law) shows that a range of composition of not less than 0.2% Co must exist if any lattice parameter change is to be detected within the limits of accuracy of the X-ray technique employed.

A typical as-cast structure is shown in figure 23. Dendrites of TiCo with peritectic rims of Ti_2Co occur in a matrix of Ti_2Co and retained β.

Figures 24 to 31 show typical annealed structures. Ti_2Co predominates in each. The second phase is α, retained β, or TiCo depending on the composition and the annealing temperature.

The only single phase structure occurred at 33.00 percent Co and 1000°C. 33.33 percent Co alloys showed a decreasing amount of TiCo as the equilibrating temperature was lowered, while the 33.15 percent Co alloy contained TiCo at 1000°C, and α at 650°C.

The metallographic results are summarized in figure 33.

DISCUSSION AND CONCLUSIONS

The X-ray results indicate that Ti_2Co has a small range of composition at high and low temperatures, and that the high temperature, form is richer in titanium than the low temperature form, since the former has the greater lattice parameter (the atomic radius of titanium is 2.91 Å; that of cobalt is 2.501 Å).

The greater lattice parameter of the high temperature form is not due to oxygen and nitrogen contamination at the higher annealing temperaure, since the sample that was equilibrated at 650°C after holding at 1000°C had the lattice parameter associated with the low temperature from of Ti_2Co. Had the alloy become contaminated, the larger parameter would have persisted after 650°C treatment.

The low temperature parameter agrees with the work of Orwell and Fontana (1), and of Duwez and Taylor (16).

The metallographic results supplement the X-ray results, and show that the range of composition is considerably less than 0.3 percent Co at 1000°C, and is centered at 33.00 percent Co. At 650°C, Ti_2Co lies between 33.15 and 33.33 percent Co.

If Vegard's law were assumed, the difference in lattice parameters would indicate that the high temperature form of Ti_2Co would occur at an even lower cobalt content. Deviations from Vegard's law are common, so this discrepancy is not surprising.

The suggested modification of the titanium-cobalt phase diagram is shown in figure 33.

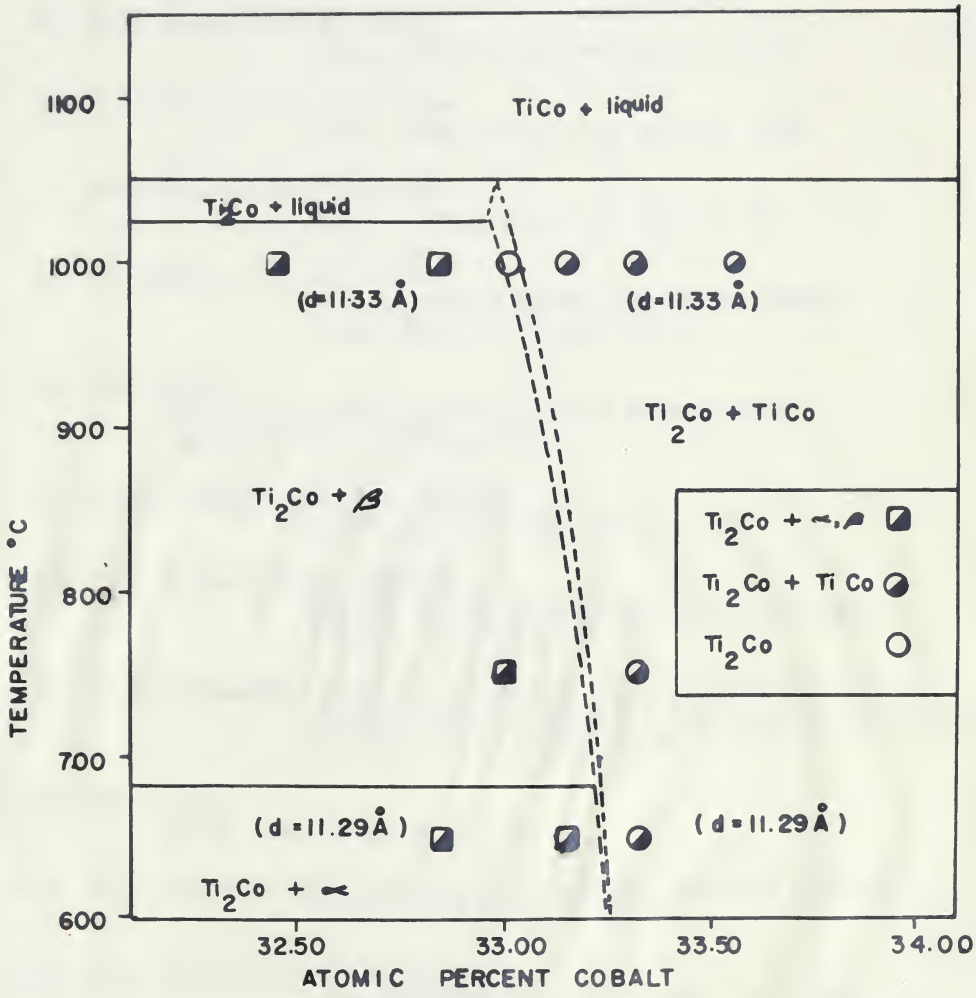

FIG. 33 PORTION OF PHASE DIAGRAM

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